Albuquerque Bernalillo County
Water Utility Authority

COMPLIANCE DIVISION
4201 2ND STREET SW, ALBUQUERQUE, NEW MEXICO 87105

WATER QUALITY LABORATORY
STANDARD OPERATING PROCEDURE APPROVAL FORM

WQL SOP 501 Metals Sample Preparation

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Out of Service By: _____ Date: / /
Reason:

History of Revision This table lists the revision history and effective dates of this procedure.

Revision	Date	Description of Changes
7	10/3/09	Complete revision to incorporate ICP/MS, remove references to specific protocols,update QC limits to latest Standard Methods, and to organize SOP according to the type of sample preparation and instrumentation rather than to the Client Protocol and type of instrumentation.

1.0 SCOPE AND APPLICATION

1.1. This SOP applies to the preparation of samples and quality control samples for analysis by WQL SOP 503, "Flame Atomic Absorption Analysis," WQL SOP 504 "Graphite Furnace Atomic Absorption Analysis," WQL SOP 505 "Inductively-Coupled Plasma/Optical Emission Spectroscopy Analysis," and WQL SOP 506 "Inductively-Coupled Plasma/Mass Spectroscopy Analysis."

1.2. All metals analyses will be conducted according to methods listed in the most current 40 CFR 136.3. Of the allowed methods in 40 CFR 136.3 the methods in Standard Methods for the Examination of Water and Wastewater Online Edition are the methods of choice for all metals preparation performed following this SOP.

NOTE: Hg sample preparation is included in WQL SOP 502 Hg by FIMS.

NOTE: For Flame analyses an acid digestion/concentration may be needed in order to achieve low detection limits.

NOTE: Turbidity measurements are performed on all Water Samples.

2.0 SUMMARY OF METHOD

2.1. This SOP describes the preparation of samples for trace metals analyses. For analyses requiring total metals analysis, samples are treated with concentrated acids and heated to dissolve available metallic elements for analysis. The method provides for controlling potential contamination sources.

2.2. The specific analytes covered by this method are provided in the applicable SOPs listed in Section 1.1. For a specific sample, the actual analytes required are determined by the client protocol which is documented in SLQ*LIMS. The Client Protocol is attached to the sample when the sample is logged into SQL*LIMS.

3.0 DEFINITION OF TERMS

3.1. **Accuracy:** Combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value.

3.2. **Analytical Batch:** Samples which are analyzed together with the same method sequence and the same lots of reagents and with the same preparation common to each sample within the same time period. The samples are of the same TYPE and the batch will be designated by sample type, protocol, revision #, year, a sequential number for the batch (restarted annually), and sample collection beginning and ending dates. **A batch consists of 20 samples or less of the same WQL protocol.**

3.3. **Calibration Blank (Cal Blk):** A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument.

3.4. **Dissolved Analyte:** The concentration of analyte in an aqueous sample that will pass through a 0.45 μm membrane filter.

3.5. **Interference:** An enhancement or depression of the atomic absorption signal of an analyte in a sample when compared with an aqueous standard of the same concentration.

3.6. **Laboratory Fortified Blank (LFB)=Laboratory Control Sample (LCS):** A regent water blank to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.7. **Laboratory Fortified Sample Matrix (LFM)=Matrix Spike (MS):** An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes positive or negative bias to the analytical results.

3.8. **Laboratory Fortified Sample Matrix Duplicate (LFM)=Matrix Spike Dup (MSD):** Two aliquot of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of MS and MSD indicate precision associated with laboratory procedure.

3.9. **Laboratory Reagent (Method) Blank (LRB):** A reagent water blank carried through the entire analytical sample preparation procedure and is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and apparatus. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the regents, or the apparatus.

3.10. **Stock Standard Solution:** A concentrated solution containing one or more method analytes prepared in the laboratory using standards purchased from a commercial source.

3.11. **Total Recoverable Metals:** Metals that can be recovered from a sample with a strong acid digestion/extraction. Standard Methods 3030C refers to these as "Extractable Metals."

4.0 INTERFERENCE

4.1. Metals sample preparation is prone to interferences from contamination. Take care not to introduce metals into samples during preliminary treatment. During pretreatment avoid contact with rubber, metal-based paints, cigarette smoke, paper tissues, and all metal products including those made of stainless steel, galvanized metal, and brass. Conventional fume hoods can contribute significantly to sample contamination, particularly during acid digestion in open containers. If contamination becomes a problem, keep vessels covered with watch glasses and turn spouts away from incoming air to reduce airborne contamination.

4.2. Plastic pipette tips often are contaminated with copper, iron, zinc, and cadmium. Avoid using colored plastics, which can contain metals. Use certified metal-free plastic containers and pipette tips when possible. Avoid using glass if analyzing for aluminum or silica if there are contamination problems with these elements. Please see section 8.1.4 for contamination control requirements for any glassware used.

4.3. Check to make sure that metal-free water is used for all operations. Check reagent-grade acids used for preservation, extraction, and digestion for purity (see Section 8.1.5 for testing requirements). If excessive metal concentrations are found, purify the acids by distillation or use ultra-pure acids. Inductively coupled plasma mass spectrometry (ICP-MS) may require use of ultra-pure acids and reagents to avoid measurable contamination.

4.4. Process blanks through all digestion and filtration steps and evaluate blank results relative to corresponding sample results as described in Sections 8.1.4 and 8.2.3.

5.0 SAFETY

5.1. **Health Hazards:** For **specific hazards**, consult the MSDS for compounds listed in section 7.0 of this SOP [MSDS on file in WQL Conference Room].

5.1.1. Use, store, and dispose of chemicals in accordance with WQL Chemical Hygiene Plan (CHP-Section 5- Revision April 2008).

5.1.2. Reagents used are potentially caustic or corrosive, avoid ingestion or inhalation and contact with the skin.

5.1.3. Digestion is to be performed under a hood. Hoods must be checked prior to sample prep, as reflected by the streamer on the glass hood face. Do not prep if hoods are not working.

5.2. **Protective Equipment:** Wear appropriate Personal Protective Equipment (PPE) in accordance with WQL CHP (Section 5.1 – Revision April 2008)

5.3. **Spills and Contamination:** Clean up spills immediately in accordance with WQL CHP (Section 5.11-Revision April 2008).

6.0 APPARATUS AND EQUIPMENT

6.1. **Hot Plates:** The temperatures of all hot plates will be recorded when in use. Temperature will be between 85-90 degrees Celsius, using 50 ml DI placed on heated hot plate to measure. Record hot plate temperatures in Sample Prep Book daily. If hot plate temperatures are not within range, report to Supervisor immediately. Corrective action will be taken before continuing use.

6.2. **Hoods:** Air flow checks will be conducted on a monthly basis by WQL personnel as stated in the WQL CHP. If hoods are not operating properly, as reflected by the streamer on the glass hood face, contact Supervisor. A repair order will be filled out. TAG OUT PROCEDURES applies to any malfunctioning hoods.

6.3. **Refrigerators:** Temperatures recorded daily by Sample Custodian. Temperature of 4-6 degrees is required. Make sure doors are always closed for effective operation. If not operating correctly report to Supervisor.

7.0 REAGENTS AND STANDARDS

7.1. **Chemicals/Reagents:** All chemicals and reagents transport and storage requirements will follow WQL QAM procedures (Section 5.6.7).

7.2. WQL Reagent Water from deionized water system. Reagent water for use following this SOP must be filtered before use.

7.3. Ultra Pure chemicals and Ultra High Purity gases or better will be used for all metals analyses. Standards will be supplied with a Certificate of Analysis showing Manufacturer's number, Description, Lot number, Expiration date, Labeled and Measured values and Traceability to NIST SRM's. Individual analytical approved methods may specify additional requirements for the reagents to be used. All reagents will be logged and dated as to the date received and date opened with the analyst's initials, follow all SOP's for chemical receiving. No chemical/reagent will be used past its expiration date. All expired reagents will be disposed of in the proper manner.

7.3.1. **HNO_3** - Ultrapure or Ultrexgrade or equivalent. For blanks and dilutions, mix 1% in reagent water to make 1% HNO_3 solution. For ICPMS blanks and dilutions, mix 2% in reagent water to make 2% HNO_3 solution.

7.3.2. **HCl** – Ultrapure or Ultrexgrade or equivalent. Mix 1 to 1 with reagent water as required by procedure.

7.3.3. **H_2O_2 30%** - Ultrapure or Ultrexgrade or equivalent.

7.4. Standard stock solutions: All standard stock solutions used will be NIST traceable following WQL QAM requirements (Section 5.6.5) for standard solutions. If NIST traceable stock solutions are not available, the solutions can be made from the pure materials as described in Standard Methods for the applicable analytical technique.

7.5. **Flame spike solutions**

7.5.1. Table 7.5-1 lists elements and recommended spike concentrations for the Spike Stock Solution and the final spiked concentrations for QC samples for flame analyses. Prepare the Spike Stock Solution by adding sufficient primary stock solutions for each element (either individually or in any combination) to create the Spike Stock Solution concentration indicated in the table.

Table 7.5-1		
Recommended Flame Spike Concentrations		
Elements	**Spike Stock Solution Concentration**	**Final Spiked Concentration in QC Samples**
Ag	50 mg/L	500 µg/L
Cr	50 mg/L	500 µg/L
Cd	50 mg/L	500 µg/L
Cu	50 mg/L	500 µg/L
Ni	50 mg/L	500 µg/L
Zn	50 mg/L	500 µg/L
Pb	50 mg/L	500 µg/L

7.5.2. For each batch of samples add 500 µL of Flame Spike Stock Solution to 50 mL of sample to create the final spike concentrations given in Table 7.5-1. This Spike Stock Solution must be added to the Matrix Spike, Matrix Spike Duplicate, Laboratory Control Sample, and Laboratory Control Sample Duplicate for each batch. It is acceptable to adjust the volume of spike added for samples and control samples prepared at other volumes, or to use stock solutions with different concentrations, to create the same final spiked concentrations.

7.6. **Furnace spike solutions**

7.6.1. Table 7.6-1 lists elements and recommended spike concentrations for the Spike Stock Solution and the final spiked concentrations for QC samples for furnace analyses. Prepare the Spike Stock Solution by adding sufficient primary stock solutions for each element (either individually or in any combination) to create the Spike Stock Solution concentration indicated in the table.

Table 7.6-1		
Recommended Furnace Spike Concentrations		
Elements	**Spike Stock Solution Concentration**	**Final Spiked Concentration in QC Samples**
Ag	0.50 mg/L	2.5 µg/L
As	5 mg/L	25 µg/L
Pb	5 mg/L	25 µg/L
Se	5 mg/L	25 µg/L
Sb	5 mg/L	25 µg/L
Tl	5 mg/L	25 µg/L
Cd	0.25 mg/L	1.25 µg/L
Cr	1.0 mg/L	5.0 µg/L

7.6.2 For each batch of samples add 250 uL of Furnace Spike Stock Solution to 50 mL of sample to create the final spike concentrations given in Table 7.6-1. This Spike Stock Solution must be added to the Matrix Spike, Matrix Spike Duplicate, Laboratory Control Sample, and Laboratory Control Sample Duplicate for each batch. It is acceptable to adjust the volume of spike added for samples and control samples prepared at other volumes, or to use stock solutions with different concentrations, to create the same final spiked concentrations.

7.7. **ICP spike solutions**

7.7.1. Table 7.7-1 lists elements and recommended spike concentrations for the Spike Stock Solution and the final spiked concentrations for QC samples for ICP analyses. Prepare the Spike Stock Solution by adding sufficient primary stock solutions for each element (either individually or in any combination) to create the Spike Stock Solution concentration indicated in the table.

Table 7.7-1

Recommended ICP Spike Concentrations for Pretreatment

Elements	Spike Stock Solution Concentration	Final Spiked Concentration in QC Samples
Al	100 mg/L	1.0 mg/L
B	100 mg/L	1.0 mg/L
Mo	100 mg/L	1.0 mg/L
Cu	100 mg/L	1.0 mg/L
Ni	100 mg/L	1.0 mg/L
Zn	100 mg/L	1.0 mg/L

7.7.2. For each batch of pretreatment samples add 500 µL of ICP Spike Stock Solution to 50 mL of sample to create the final spike concentrations given in Table 7.6-1. This Spike Stock Solution must be added to the Matrix Spike, Matrix Spike Duplicate, Laboratory Control Sample, and Laboratory Control Sample Duplicate for each batch. It is acceptable to adjust the volume of spike added for samples and control samples prepared at other volumes, or to use stock solutions with different concentrations, to create the same final spiked concentrations.

7.7.3. Table 7.7-2 lists elements and recommended spike concentrations for the Spike Stock Solutions 1 through 4 and the final spiked concentrations for QC samples for undigested ICP analyses. Prepare the Spike Stock Solution by adding sufficient primary stock solutions for each element (either individually or in any combination) to create the Spike Stock Solution concentration indicated in the table.

Table 7.7-2 Recommended ICP Spike Concentrations for Waters (undigested)			
Standard ID	**Elements**	**Spike Stock Solution Concentration**	**Final Spiked Concentration in QC Samples**
1	Al	10 mg/L	0.77 mg/L
1	Ba	10 mg/L	0.77 mg/L
1	Be	10 mg/L	0.77 mg/L
1	Ca*	10 mg/L	0.77 mg/L
1	Co	10 mg/L	0.77 mg/L
1	Cu	10 mg/L	0.77 mg/L
1	Fe	10 mg/L	0.77 mg/L
1	K*	10 mg/L	0.77 mg/L
1	Li	10 mg/L	0.77 mg/L
1	Mg*	10 mg/L	0.77 mg/L
1	Mn	10 mg/L	0.77 mg/L
1	Ni	10 mg/L	0.77 mg/L
1	Na*	10 mg/L	0.77 mg/L
1	Ag	10 mg/L	0.77 mg/L
1	Sr	10 mg/L	0.77 mg/L
1	V	10 mg/L	0.77 mg/L
1	Zn	10 mg/L	0.77 mg/L
2	B	10 mg/L	0.77 mg/L
2	Mo	10 mg/L	0.77 mg/L
3	Ca*	500 mg/L	38.5 mg/L
3	Na*	500 mg/L	38.5 mg/L
3	K*	100 mg/L	7.7 mg/L
3	Mg*	100 mg/L	7.7 mg/L
4	Si**	1,000 mg/L	10.0 mg/L
***Ca has a total concentration of 51 mg/L**			
***Na has a total concentration of 51 mg/L**			
***K has a total concentration of 11 mg/L**			
***Mg has a total concentration of 11 mg/L**			
****Si is reported as SiO2. Multiply final spiked concentration by 2.14 to convert Si concentration to SiO2 concentration. This gives a total concentration in the spiked samples of 21.4 mg/L**			

7.7.4. For each batch of undigested water samples add 2,500 µL of each ICP Spike Stock Solutions 1, 2, and 3 listed in Table 7.7-2 to 25 mL of sample to create the final spike concentrations given in Table 7.7-2. This Spike Stock Solution must be added to the Matrix Spike, Matrix Spike Duplicate, Laboratory Control Sample, and Laboratory Control Sample Duplicate for each batch. It is acceptable to adjust the volume of spike added for samples and control samples prepared at other volumes, or to use stock solutions with different concentrations, to create the same final spiked concentrations.

7.7.5. In addition, for the Si QC samples, prepare a separate set of QC samples (Matrix Spike, Matrix Spike Duplicate, Laboratory Control Sample, and Laboratory Control Sample Duplicate) by adding 500 µL of ICP Spike Stock Solution 4 (Si spike standard) to 50 mL to achieve 10 mg/L final spiked concentration.

7.7.6. Table 7.7-3 lists elements and recommended spike concentrations for the Spike Stock Solutions 1 through 4 and the final spiked concentrations for QC samples for digested ICP analyses. Prepare the Spike Stock Solution by adding sufficient primary stock solutions for each element (either individually or in any combination) to create the Spike Stock Solution concentration indicated in the table.

Table 7.7-3 Recommended ICP Spike Concentrations for Waters (digested)			
Standard ID	**Elements**	**Spike Stock Solution Concentration**	**Final Spiked Concentration in QC Samples**
1	Al	10 mg/L	0.5 mg/L
1	Ba	10 mg/L	0.5 mg/L
1	Be	10 mg/L	0.5 mg/L
1	Ca*	10 mg/L	0.5 mg/L
1	Co	10 mg/L	0.5 mg/L
1	Cu	10 mg/L	0.5 mg/L
1	Fe	10 mg/L	0.5 mg/L
1	K*	10 mg/L	0.5 mg/L
1	Li	10 mg/L	0.5 mg/L
1	Mg*	10 mg/L	0.5 mg/L
1	Mn	10 mg/L	0.5 mg/L
1	Ni	10 mg/L	0.5 mg/L
1	Na*	10 mg/L	0.5 mg/L
1	Ag	10 mg/L	0.5 mg/L
1	Sr	10 mg/L	0.5 mg/L
1	V	10 mg/L	0.5 mg/L
1	Zn	10 mg/L	0.5 mg/L
2	B	10 mg/L	0.5 mg/L
2	Mo	10 mg/L	0.5 mg/L
3	Ca*	500 mg/L	25 mg/L
3	Na*	500 mg/L	25 mg/L
3	K*	100 mg/L	5.0 mg/L
3	Mg*	100 mg/L	5.0 mg/L
4	Si**	1,000 mg/L	10.0 mg/L
*Ca has a total concentration of 25.5 mg/L			
*Na has a total concentration of 25.5 mg/L			
*K has a total concentration of 5.5 mg/L			
*Mg has a total concentration of 5.5 mg/L			
**Si is reported as SiO2. Multiply final spiked concentration by 2.14 to convert Si concentration to SiO2 concentration. This gives a total concentration in the spiked samples of 21.4 mg/L			

7.7.7. For each batch add 2,500 µL of each ICP Spike Stock Solutions 1, 2, and 3 listed in Table 7.7-3 to a final volume of 50 mL for the preparation of the MS, MSD, LCS, and LCSD. This will provide the final spike concentrations given in Table 7.7-3. It is acceptable to adjust the volume of spike added for samples and control samples prepared at other volumes, or to use stock solutions with different concentrations, to create the same final spiked concentrations.

7.7.8. In addition, for the Si QC samples, prepare a separate set of QC samples (Matrix Spike, Matrix Spike Duplicate, Laboratory Control Sample, and Laboratory Control Sample Duplicate) by adding 500 µL of ICP Spike Stock Solution 4 (Si spike standard) to 50 mL to achieve 10 mg/L final spiked concentration.

7.8. **ICPMS spike solution**

7.8.1. ICPMS Spike Stock Solution (See Table 7.8-1 for elements, Spike Solution Concentration, and final spike concentration in QC samples). Prepare the Spike Stock Solution by adding sufficient primary stock solutions for each element (either individually or in any combination) to create the Spike Stock Solution concentration indicated in the table. For Selenium, a higher spike level is used due to the lower sensitivity for selenium, as allowed by the method.

Table 7.8-1

ICPMS Spike Solution 1

Elements	Spike Stock Solution Concentration	Final Spiked Concentration in QC Samples
Aluminum	20 mg/L	100 µg/L
Antimony	20 mg/L	100 µg/L
Arsenic	20 mg/L	100 µg/L
Barium	20 mg/L	100 µg/L
Beryllium	20 mg/L	100 µg/L
Cadmium	20 mg/L	100 µg/L
Chromium	20 mg/L	100 µg/L
Copper	20 mg/L	100 µg/L
Cobalt	20 mg/L	100 µg/L
Lead	20 mg/L	100 µg/L
Manganese	20 mg/L	100 µg/L
Molybdenum	20 mg/L	100 µg/L
Nickel	20 mg/L	100 µg/L
Selenium	20 mg/L	100 µg/L
Silver	20 mg/L	100 µg/L
Thallium	20 mg/L	100 µg/L
Vanadium	20 mg/L	100 µg/L
Zinc	20 mg/L	100 µg/L

* Selenium is in both stock solutions used. The multi-element stock solution has Se at 20 µg/L and the Se-only stock solution has Se at 100 µg/L. Combined this gives the 300 ug/L final spiked concentration.

7.8.2 For each batch add 250 µL of the multi-element ICP Spike Stock Solution and 100 µL of the Se-only spike solution listed in Table 7.8-1 to a final volume of 50 mL for the preparation of the MS, MSD, LCS, and LCSD. This will provide the final spike concentrations given in Table 7.8-1. It is acceptable to adjust the volume of spike added for samples and control samples prepared at other volumes, or to use stock solutions with different concentrations, to create the same final spiked concentrations.

NOTE: For undigested water samples for ICPMS, the final spiked concentration is 99.5 µg/L since the final volume will be increased by the 250 µL of ICPMS Spike Solution added to give a final volume of 50.25 mL. The final concentration for Se in undigested waters is 298 µg/L since the final volume will be increased by the 350 µL of Spike Solutions added to give a final volume of 50.35 mL.

8.0 QUALITY ASSURANCE/ QUALITY CONTROL

8.1. Quality Assurance

8.1.1. **Analyst Training:** Analysts must follow the steps outlined in the DOC Training program for WQL SOP's. Follow requirements in QA SOP-004.

8.1.2. **Quality Control Requirements:** Follow requirements in QA SOP-005. The quality control requirements section covers the following topics: 1) Quality control limits 2) Quality control - instrument performance 3) Laboratory (Method).

8.1.3. **Data Evaluation:** Follow requirements in QA SOP-005. The Data Evaluation section covers the following topics: 1) Internal audits 2) Control charts procedures 3) performance audits 4) Method detection limit procedures.

8.1.4. **Contamination:** The following precautions contribute to avoid inorganic contaminants.

8.1.4.1. Safety Practices: General and customary safety practices as well as those included in instrument manufacturer's manuals and approved methods will be strictly followed. Material Safety Data Sheets will be consulted before using any new or unknown chemical/reagent.

8.1.4.2. All glassware used for metals analyses will be separate from all other in the Lab and be specified as such. Only Class A Volumetric glassware will be used. All glassware will be cleaned according to the following procedure:

8.1.4.3. **Between Sample Transfers:**

8.1.4.3.1. Rinse with 1:1 nitric acid.
8.1.4.3.2. Rinse with filtered DI water.
8.1.4.3.3. Rinse with sample.

8.1.4.4. **After use:**

8.1.4.4.1. Wash with detergent (Alconox or Contrad), by hand or in pipet washer, as appropriate.
8.1.4.4.2. Rinse with tap water.
8.1.4.4.3. Rinse with 1:1 nitric acid.
8.1.4.4.4. Rinse with filtered DI water 2X.
8.1.4.4.5. Place in rack and cover.

8.1.5. **Acid Testing:** Analysis of a HNO_3 and HCl blank will be analyzed with every new lot of acid prior to usage. Upon receipt, a sample of each new acid lot is tested for metals content using GFAA, ICP, or ICPMS, as appropriate before being used for preparations for analysis on these instruments. This will evaluate any possible contamination due to the acids used. Record this testing in the Acids Logbook before placing the new lot of acid into use.

8.1.6. **Containers:** Use metal free containers for all prepped samples. Certification provided by the supplier indicating the containers are metal free must be stored in the QA files.

8.2. **Quality Control:**

8.2.1. **Quality Control Requirements:** The minimum requirements of this QC program consist of an initial demonstration of laboratory capability, and periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

8.2.2. Sample matrix spike/matrix duplicate analyses:

8.2.2.1. Prepare sample, sample matrix spike (MS) and sample matrix spike duplicate (MSD) as described in Section 7 for the appropriate analysis.

8.2.2.2. Control limits:

8.2.2.2.1. 75% to 125% recovery

8.2.2.2.2. 20% RPD

8.2.2.3. Frequency - One each per batch of 20 samples

8.2.2.4. Check – Spike prep, sample prep, and documentation

8.2.2.5. Record – Text affected samples with MS/MSD

8.2.3. Laboratory Reagent (Method) Blank (LRB)

8.2.3.1. Reagent water.

8.2.3.2. Control Limits – Concentration should be less than MDL.

8.2.3.3. Frequency - Each batch of 20 or fewer samples.

8.2.3.4. Corrective Action - When LRB values constitute 10% or more of the analyte level determination for a sample or is greater than the Reporting Limit, whichever is greater (essentially the LRB result must be less than 10% of the lowest sample result for the associated batch or less than the reporting limit), fresh aliquots of the samples must be prepared and analyzed for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

8.2.3.5. Check - Laboratory or reagent contamination should be suspected.

8.2.3.6. Record - Corrective actions in logbook.

8.2.4. Laboratory Control Sample (LCS)

8.2.4.1. Control Limits - Recovery 70-130%, or as determined by control charts.

8.2.4.2. Frequency - One LCS per batch.

8.2.4.3. Corrective Action – Rerun LCS/LCSD one time to determine if second analysis meets criteria. If not, implement corrective action procedure to identify root cause.

8.2.4.4. Check - Spike solution and sample prep technique

8.2.4.5. Record - Corrective Action Response Report must be initiated for all LCS failures.

8.2.4.6. Control Chart -Verification of laboratory performance done for each analyte.

8.2.5. Laboratory Control Sample Duplication (LCSD)

8.2.5.1. Analyte concentration must be the same as that used in the LCS.

8.2.5.2. Control Limits - Percent difference of +/-20% between LCS & LCSD and Recovery 70-130%, or as determined by control charts.

8.2.5.3. Frequency - One per batch of 20 samples or less

8.2.5.4. Corrective Action – Rerun LCS/LCSD one time to determine if second analysis meets criteria. If not, implement corrective action procedure to identify root cause.

8.2.5.5. Check - Spike solution and sample prep technique

8.2.5.6. Record – Corrective Action Response Report must be initiated for all LCS failures.

8.2.6. Low-level Standard (LLS)

8.2.6.1. Analyte concentrations should be ± 50% or ± the reporting limit of true value, whichever is greater.

8.2.6.2. Corrective action – Text all results between the reporting limit and the low standard as estimated due to inaccuracy in the LLS.

9.0 PROCEDURE

9.1. Sample Handling

9.1.1. **Preservation** – All samples will be prepared following Standard Operating Procedures Sample Preparation Manual. Samples preserved with the addition of 2.5ml HNO_3. For mercury samples 2.5 mL HNO_3 and 5.0 H_2SO_4 is used for preservation. All mercury and sludge or other solid samples will be stored in the spectroscopy refrigerator, in the sample preparation area, until analysis. Aqueous samples for metal components other than mercury may be stored at ambient (room) temperature.

9.1.2. **Sample Holding Time** – Holding time for mercury samples is 28 days. Holding time for all other metal components is six months.

9.1.3. **Storage** – Samples that may have legal ramifications due to not being within regulatory compliance limits are to be stored in a secure area but for no longer than their allowed holding times. Confer with the supervisor before discarding any samples.

9.2. Liquid Sample Dissolved Metals Preparation Procedure for FLAME, FURNACE, ICP, and ICPMS

9.2.1. Samples are received **FILTERED** and **ACIDIFIED**. Sample custodian will check proper labeling and acidification.

NOTE: The process control sample does come in directly from the plant. For this sample, it must be filtered and acidified before analysis.

9.2.2. Reference: Online Edition of Standard Methods, Part 3030C, PRELIMINARY TREATMENT OF SAMPLES.

9.2.3. Prepare batch QC samples as described in section 8.2 using the instrument-specific spiking solutions described in sections 7.5 (Flame), 7.6 (Furnace), 7.7 (ICPOES), and 7.8 (ICPMS).

9.2.4. 50 mL of the well mixed, filtered, acidified sample from the original container is poured directly into a new disposable 50 mL metal free conical test tube.

9.2.5. Add 3-5 drops of conc. Ultra pure HNO3 with the dropper.

9.2.6. Mark test tube as 1XFA (Filtered Acidified Straight).

9.2.7. Record the following on the Sample Preparation Logsheet for each sample.

9.2.7.1. Date of preparation.

9.2.7.2. Analyst prepping.

9.2.7.3. Lot numbers of HNO3

9.2.7.4. Amount of spike standard used, and

9.2.7.5. Standard reference numbers.

9.2.8. All metals analytical results will be reported as DISSOLVED.

9.3. **Liquid Sample Total Recoverable Metals Preparation Procedure for FLAME, FURNACE, ICP, and ICPMS**

NOTE: If the sample contains undissolved solids >1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid mixture procedure described in Sections 9.3.

9.3.1. Samples should be received Acidified to a pH of less than 2. Sample custodian will check proper labeling and acidification.

9.3.2. Reference: Online Edition of Standard Methods, Part 3030D, PRELIMINARY TREATMENT OF SAMPLES.

9.3.3. Prepare batch QC samples as described in section 8.2 using the instrument-specific spiking solutions described in sections 7.5 (Flame), 7.6 (Furnace), 7.7 (ICPOES), and 7.8 (ICPMS).

9.3.4. All metals analytical results will be reported as TOTAL.

9.3.5. A 50 mL aliquot of the well mixed, acidified sample from the original container is volumetrically transferred using a certified class A 50 mL graduated mixing cylinder to a 250 mL beaker.

9.3.6. Add 2.5 mL of ultra pure HNO3.

9.3.7. The sample is placed on a thermostatically controlled hot plate and allowed to gently reflux without vigorously boiling or let go to dryness, to a volume of approximately 10 mL. See Section 6.2 for temperature requirements.

9.3.8. The sample is allowed to cool then carefully poured into a 50 mL certified class a graduated cylinder. Wash down beaker walls with at least three portions of filtered DI water, adding these rinsing to the graduated cylinder.

9.3.9. The sample is then brought back to the original volume of 50 mL by carefully adding filtered DI water.

9.3.10. The sample is thoroughly mixed and poured into a new disposable 50 mL metal free conical centrifuge tube.

9.3.11. Mark conical tube as 1XD

9.3.12. Record the following in the Sample Preparation Book for each sample.

9.3.12.1. Date of preparation.

9.3.12.2. Analyst prepping.

9.3.12.3. Temperature of hot plate.

9.3.12.4. Lot numbers of HNO3

9.3.12.5. Amount of spike standard used, and

9.3.12.6. Standard reference numbers.

9.4. **Solid Sample Total Recoverable Metals Preparation Procedure for FLAME, FURNACE, ICP, and ICPMS**

9.4.1. Reference: Online Edition of Standard Methods, Part 3030, PRELIMINARY TREATMENT OF SAMPLES.

9.4.2. Five analytical techniques may be employed: **FIMS, FLAME, FURNACE, ICP, and ICPMS.**

9.4.3. Prepare batch QC samples as described in section 8.2 using the instrument-specific spiking solutions described in sections 7.5 (Flame), 7.6 (Furnace), 7.7 (ICPOES), and 7.8 (ICPMS).

9.4.4. A representative sample (10 grams) of as received wet sludge is placed in a teflon dish and dried at 60 degrees C until any moisture or liquid portion has completely evaporated which can be determined by the samples flaky appearance.

9.4.5. The entire dried solid fraction is ground in a GLASS mortar to achieve homogeneity and then transferred to a 30 ml disposable glass Test Tube, capped and labeled. Do not use porcelain mortar as they have shown to be contaminated with lead and cadmium.

9.4.6. A 0.25 gram sample of the ground dried sludge is then transferred to a 125 ml erlenmeyer flask, 10 ml of Ultrapure Nitric Acid added, covered and placed on a hot plate at 95 degrees C and refluxed WITHOUT BOILING for 10 minutes.

9.4.7. Remove from the hot plate and allow to cool, add 5 ml of concentrated Ultrapure Nitric Acid, cover and again reflux WITHOUT BOILING for 30 minutes.

9.4.8. Remove from the hot plate and allow to cool, add an additional 5 ml of concentrated Ultrapure Nitric Acid and again reflux and evaporate WITHOUT BOILING or allowing the sample to go to dryness to approximately 5 ml.

9.4.9. Remove from the hot plate and allow to cool, add 2 ml of filtered DI water and 3 ml of Ultrapure 30% Hydrogen Peroxide, cover, and return to the hot plate and heat until any effervescence subsides.

9.4.10. The digested sample is then filtered with 3 digestion flask washings with filtered DI using an HNO3 acid washed Whatman No. 41 or equivalent 7 cm filter and brought up to a final volume of 100 ml with filtered DI water using a class A graduated mixing cylinder.

9.4.11. Mix the sample well and transfer 50 ml aliquot to a metal free labeled 50 ml conical centrifuge tube for **FLAME, FURNACE,** and **ICP** analyses .

9.4.12. The remaining 50 ml in the mixing cylinder is diluted to 100 ml with filtered DI water, mixed and transferred to a 250 ml disposable snap cap container, 2.5 ml HNO3 and 5 ml H2SO4 added. Analyze for Mercury with 28 days.

10.0 DATA REPORTING

10.1 **Calculations** – Provide a list of calculations used in this method

10.2 **Logbook entry** – Describe the information written on the logbook form. Refer to the logbook attachment

10.3 **Corrective actions** – Follow requirements in QA SOP-003 and A SOP-005. The corrective actions section covers the following topics: 1) Out of control data procedures 2) Corrective action logbooks

10.4 **Data assessments** – in QA SOP-005. The data assessments section covers the following topics: 1) Accuracy and precision 2) Data validation procedures 3) Data reporting procedures.

11.0 MAINTENANCE

11.1. Provide a list of daily, weekly, and monthly maintenance required for this method. Refer to maintenance logbook form.

12.0 TROUBLESHOOTING

12.1. List any troubleshooting information in this section.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1. All waste disposal procedures will follow the Water Quality Laboratory CHP (Section 5.12-Revision April 2008). Disposal procedure is as follows:

13.1.1 Discard all remaining analyzed samples in an acid sink.

13.1.2 All sample lab-ware must be washed with laboratory soap inside and out followed by multiple rinses with distilled or deionized water.

13.1.3 Pollution Prevention - Eliminate waste at the source and base the quantity of purchase reagents on expected usage during their shelf life.

14.0 REFERENCES

14.1. Online Edition of Standard Methods, Part 3030, PRELIMINARY TREATMENT OF SAMPLES.